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A NEW LIGHT: Investigating the Luminescence of $Ba_7F_{12}Cl_2$:Eu^{2+}

Introduction

$Ba_7F_{12}Cl_2$:Eu^{2+} luminesces when excited with UV light. It is a candidate for use in LEDs, as its luminescence is white and thus renders colors more accurately than tinted or mixed light. Also, because its excitation wavelengths lie around 350nm, $Ba_7F_{12}Cl_2$:Eu^{2+} would be more energy-efficient than phosphors needing to be excited at shorter wavelengths. Finally, $Ba_7F_{12}Cl_2$:Eu^{2+} is an interesting target for research because its luminescence results from interactions between the three lattice sites for Eu^{2+} in the Ba7F12Cl2 crystal.
To develop $Ba_7F_{12}Cl_2$:Eu^{2+} for LEDs, we first need to know how its luminescence can be influenced and adjusted. In this project, I wanted to investigate the influences of temperature, Eu^{2+} concentration, and excitation wavelength on $Ba_7F_{12}Cl_2$:Eu^{2+} luminescence.

Methods

Samples were synthesized from BaF_2, LiCl, KCl and EuF_2. In total, six samples with Eu^{2+} concentrations of 0.015%, 0.1%, 0.37%, 0.9%, 1.8%, and 3.7% were used in the experimental measurements.
To determine the influence of excitation wavelength on the luminescence, emission spectra of all samples were measured with a fluorimeter at excitation wavelengths of 275nm, 300nm, 320nm, 340nm, 360nm and 380nm.
Temperature-dependent measurements were performed on a sample with an Eu^{2+} concentration of 0.9%. The sample was placed in a cryostat. It was excited at 320nm and its emission spectra measured for sample temperatures between 5K and 300K.
The luminescence decay time was measured on three samples with respective Eu^{2+} concentrations of 0.1%, 0.9% and 3.7%. The samples were excited at 355nm. Decay time measurements were repeated on the 0.9% sample at temperatures of 100K, 200K and 300K. Emission spectra of the 0.1% and 3.7% samples were measured at an excitation wavelength of 266 nm and a temperature of 5K.
All spectra were processed and analyzed using the data program IGOR.

Results

I found that Eu^{2+} concentration influences luminescence in that it affects the activity of the three Eu^{2+} lattice sites: at high Eu^{2+} concentrations, energy transfer between lattice sites favor emission from the low-energy sites. As a result, the wavelength of luminescence shifts from 450nm to 550nm, appearing «warmer».
The decay time of luminescence is 2.5µs or lower depending on the measured wavelength. It isn't affected by changes in Eu^{2+} concentration. This result is unexpected: if energy is transferred from a state A to a state B with increasing concentration, the lifetime of state A becomes shorter. The observation of an initial increase of the emission intensity indicates that the emitting state is not directly excited by the laser.
The temperature-dependent measurements suggest that higher temperatures favor energy transfer between lattice sites, again resulting in a «warmer» luminescence from low-energy sites. The decay time is not affected by temperature variations.
Exciting $Ba_7F_{12}Cl_2$:Eu^{2+} at different wavelengths reveals that wavelengths around 300nm are most effective at exciting the high-energy lattice sites. Luminescence of longer wavelengths tends to be red-shifted and has a longer decay time than luminescence of short wavelengths. Curve fitting performed on the decay time spectra shows that short-wavelength light is emitted from a single lattice site, while light of longer wavelengths is emitted following energy transfer between lattice sites.

Discussion

Due to the large number of samples with different Europium concentrations and the wide range of sample temperatures, I could perform an extensive comparison between results. The shift of $Ba_7F_{12}Cl_2$:Eu^{2+} luminescence to «warmer» or «cooler» wavelengths depending on temperature and Eu^{2+} concentration is promising for its use in LEDs, since the color of luminescence can be fine-tuned by varying these parameters.
The fact that Eu^{2+} concentration doesn't influence the luminescence decay time can't be explained by a simple energy-transfer model. Further measurements suggest that energy is transferred within the crystal from «normal» (Eu^{2+}) to «anomalous» (Eu^{3+} and trapped electron) states. This is an exciting extension of our understanding of the crystal's luminescence mechanism.

Conclusions

Eu^{2+} concentration and temperature can be used to fine-tune the wavelength of luminescence. In this sense, I confirmed that $Ba_7F_{12}Cl_2$:Eu^{2+} has promise as an LED phosphor. The observation of the presence of a more complex energy transfer mechanism than anticipated raises questions that encourage further research.